

PATENT ABSTRACTS OF JAPAN

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(54) THICK-FILM RESISTOR FORMING PASTE

(57)Abstract:

PURPOSE: To provide a thick-film resistor forming paste which has almost the same electrical characteristics as the conventional one and is inexpensive than the conventional one.

CONSTITUTION: A thick-film resistor forming paste is substantially formed of conductive particles, a glass frit and an organic vehicle. The conductive particle is rhenium oxide, the surface of which particle is covered partly or wholly with a coating layer composed of one or two kinds selected from ruthenium oxide, iridium oxide and rhodium oxide.

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CLAIMS

[Claim(s)]

[Claim 1] The paste for thick film resistor formation characterized by being the rhenium oxide particle by which some or all on the front face of a particle is covered with the enveloping layer which said conductive particle becomes from a kind of ruthenium oxide, iridium oxide, and the rhodium oxide, or two sorts in the paste for thick film resistor formation constituted substantially with a conductive particle, a glass frit, and an organic vehicle.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the paste used in order to form the resistor element of a hybrid IC or a thick-film chip.

[0002]

[Description of the Prior Art] Although used cheaply [the thick film resistor component in an electronic ingredient], and easily extensively from there being high-reliability, current [which industrial engineering has established mostly], and the thing which can be supplied increasingly with high quality and at a low price are required. This thick film resistor only prints and calcinates the paste for thick film resistor formation on a substrate, and can form the resistor element in a circuit. This paste consists of substantially organic vehicles added in order to make a conductive particle, a glass frit, and them into the shape of a paste suitable for printing. In almost all cases, in the actual condition, lead borosilicate system glass, such as lead borosilicate glass ($\text{PbO-SiO}_2\text{-B}_2\text{O}_3$) and alumino lead borosilicate glass ($\text{PbO-SiO}_2\text{-B}_2\text{O}_3\text{-aluminum } 2\text{O}_3$), is used for the glass frit for a diacid-ized ruthenium (RuO_2) or Ru system pyrochlore ($\text{Bi}_2\text{Ru}_2\text{O}_7\text{-X}$, $\text{Pb}_2\text{Ru}_2\text{O}_7\text{-X}$) as a conductive particle.

[0003] Ru system oxide is used as a conductive particle because the relation (loading curve) of the electric resistance value over conductive particle weight mainly changes gently-sloping. Lead borosilicate system glass is used for a glass frit because a coefficient of thermal expansion is suitable for it of an alumina substrate and near, viscosity and the temperature dependence of surface tension, the wettability of RuO_2 , etc. are suitable for this paste system. this basic presentation -- in addition, adjustment of the temperature coefficient (TCR) of resistance, printing nature, the trimming nature by laser, the printing sagging nature at the time of baking, adhesion with a substrate, and a conductor -- various additives were added in consideration of the difference of reactivity with an electrode, and an expansion coefficient with coat glass etc., and the paste of varieties has so far been developed dramatically.

[0004] The ruthenium oxide of the electrical property being recognized as a fault of Ru system resistive paste as a problem of another dimension for many years is an expensive thing compared with glass or the usual oxide raw material. Although there are iridium, a rhodium, etc. as an element which can be replaced with a ruthenium in property, these are still more expensive than a ruthenium. Although the cutback of cost was completed when the conductive particle cheaper than this could be substituted for the whole ruthenium oxide or a part, without reducing electrical characteristics, such [until now] an effective alternative was not known.

[0005]

[Problem(s) to be Solved by the Invention] Conventionally, the technical problem of this invention has electrical characteristics almost the same as elegance, and they are to offer the cheap paste for thick film resistor formation compared with elegance conventionally.

[0006]

[Means for Solving the Problem] This invention is in the paste for thick film resistor formation characterized by being the rhenium oxide particle by which some or all on the front face of a particle is covered with the enveloping layer which said conductive particle becomes from a kind of ruthenium oxide, iridium oxide, and the rhodium oxide, or two sorts in the paste for thick film

resistor formation constituted substantially with a conductive particle, a glass frit, and an organic vehicle.

[0007] The organic vehicle for printing and additives other than these are used for the conductive particle of this paste for thick film resistor formation, and a glass frit list by the same blending ratio of coal as the conventional paste for thick film resistor formation.

[0008] the conductive particle used by this invention -- a rhenium oxide (Re_2O_3 , or ReO_2 , ReO_3 and Re_2O_7) particle -- a subject -- carrying out -- and the particle front face -- ruthenium oxide, iridium oxide, rhodium oxide, and ** -- it is characterized by being the structure where the whole or part was covered with an inner kind or two sorts or more. this invention -- a ruthenium oxide -- ruthenium oxide (namely, RuO_2 , RuO_3 , or RuO_4) and ruthenium system pyrochlore (namely, $\text{Pb}_2\text{Ru}_2\text{O}_7\text{-X}$ --) $\text{Bi}_2\text{Ru}_2\text{O}_7\text{-X}$, $\text{Ti}_2\text{Ru}_2\text{O}_7$, etc. -- containing -- iridium oxide -- oxidation iridium (namely, Ir_2O_3 or IrO_2) and iridium system pyrochlore (namely, $\text{Pb}_2\text{Ir}_2\text{O}_7\text{-X}$ --) With rhodium oxide, an oxidation rhodium (namely, Rh_2O_3 , RhO_2 , or RhO_3) and rhodium system pyrochlores ($\text{Pb}_2\text{Rh}_2\text{O}_7\text{-X}$, $\text{Bi}_2\text{Rh}_2\text{O}_7\text{-X}$, $\text{Ti}_2\text{Rh}_2\text{O}_7$, etc.) shall be included, including $\text{Bi}_2\text{Ir}_2\text{O}_7\text{-X}$, $\text{Lu}_2\text{Ir}_2\text{O}_7$, etc.

[0009] A glass frit is used that what is necessary is just to make into a subject the lead borosilicate glass used for the usual paste for thick film resistor formation, being corrected to the presentation which usually contains an alumina, a zinc oxide, calcia, a titania, the barium oxide, etc. in this ternary system.

[0010] The conductive particle of this invention forms the thin film of Ru, Ir, or Rh in a rhenium oxide particle front face by vacuum evaporatio, sputtering, etc., heats this and forms an oxide film. Furthermore, it can obtain also by dry type or wet ball mill mixing. For example, a zirconia ball etc. may be used as a churning medium, and the usual water flat tip ball mill mixing may be performed without existence under existence of a distributed solvent, and the mixed high mill of the mechanical pressure of vibration mills, such as SPEX (Sytech Corporation), the attritor mill (Union Process Inc.) of Szegrevi which carries out electric churning compulsorily with agitator feather, etc. may be used.

[0011] When using a vibration mill and an attritor mill, in addition to rhenium oxide powder, a kind of ruthenium oxide, oxidation iridium, an oxidation rhodium, ruthenium system pyrochlore, iridium system pyrochlore, and the rhodium system pyrochlores or two sorts or more are mixed, a ceramic and the hard ball made from stainless steel are used, and compulsive churning mixing is performed for dry type or water, or alcohol with a little ***** wet.

[0012] Moreover, when there are few amounts of solvents which add the case where it carries out by dry type, and wet, in consideration of that a conductive particle is expensive, friction by agitator feather, or churning nature, the glass frit added to a conductive particle may be beforehand mixed at this process.

[0013]

[Function] Since oxidation will progress to Re_2O_7 on the way, this will sublime at low temperature (250 degrees C) and a rhenium component will be lost if it mixes with glass and heats by independent [its], after calcinating rhenium oxide at an elevated temperature, the conductivity as a resistor of it will almost be lost. However, after attaching the film for a ruthenium compound, an iridium compound, or a rhodium compound by vacuum evaporatio or the spatter, by oxidizing these film, the part into which a rhenium oxide particle front face comes into contact with atmospheric air or a vehicle decreases, volatilization of a rhenium component is suppressed during baking, and it becomes possible to use it as a conductive component of the paste for thick film resistor formation.

[0014] Moreover, a rhenium oxide particle is covered by particles, such as a diacid-ized ruthenium with the fine front face of a rhenium oxide particle, when performing ball mill mixing with particles, such as ruthenium oxide, oxidation iridium, an oxidation rhodium, ruthenium system pyrochlore, iridium system pyrochlore, and rhodium system pyrochlore. Furthermore, when mixing with the ball mill by which powerful churning, such as a vibration mill and attritor, was accompanied, some rhenium atoms refuse association with oxygen, it may become a metal cluster, or it may permute by a ruthenium atom etc. and a rhenium oxide front face may deteriorate to the structure of $\text{O}(\text{Re}, \text{Ru})_2$ grade.

[0015] Therefore, the metal of a rhenium oxide particle surface layer or a cluster condition which

stored many distortion promotes Re to the inside of glass, and diffusion of Ru, the distributed condition of a conductive particle becomes good, and it has good effect also on electrical properties, such as a noise, at the same time volatilization of a rhenium component is suppressed during baking. [0016] Moreover, in adding a glass particle and carrying out ball mill mixing with this, while condensation of rhenium oxide or a diacid-ized ruthenium can be taken with the mechanical pressure which joins a conductive particle and dispersibility becomes good by the glass particle, when a high energy mill is used, the temperature of a contact part rises, and a part of rhenium and ruthenium carry out ** ON into a glass particle as microscopic grains or a cluster according to this heat mechanical effectiveness. If a glass frit with such the special fine structure is used for a paste, the noise of a resistor element is reduced and electrical strength can be improved.

[0017] as mentioned above -- without, as for each rhenium oxide particle covered with oxides, such as a ruthenium, iridium, and a rhodium, in the front face, electric conductivity falls -- moreover -- the time of paste baking -- the glass matrix from these particles -- turning -- diffusion of a rhenium or a ruthenium -- usually -- a paste and an EQC -- or since it is carried out more than it, dispersibility goes up, a noise is reduced and the resistor using this shows a good resistor property, though cheap quality of an alternative called rhenium oxide is used.

[0018]

[Example]

15g [of powder of example 1 rhenium oxide (Re_2O_3)], 5g [of powder of a diacid-ized ruthenium (RuO_2)], and ethyl alcohol 8ml was put into the plastic envelope with zirconia ball 150g, and level ball mill mixing was performed for seven days. This was filtered, it dried and surface treatment rhenium oxide / diacid-ized ruthenium mixed powder was obtained. When embedding of this powder was carried out to n-butyl methacrylate resin, the resin piece which includes a powdered cross-section slice by the ultramicrotome (ULTRACUT-E) made from Reichert-Jung was produced and this was observed with the acceleration voltage of 200kV with the JEM[by JEOL Co., Ltd.]-2000EX mold transmission electron microscope, another structure of seeming a diacid-ized ruthenium near the front face of a rhenium oxide particle was observed.

[0019] The organic vehicle which uses glass frit 18g, and the ethyl cellulose and the terpineol of the presentation of 55.4(all %s express weight % below) % PbO -24.7% SiO_2 -12.3%B-2O3-8.5% aluminum 2O3 by weight % to 2g of this powder as a principal component was used as resistive paste so that it might become 30% of the weight of the whole. This was screen-stenciled in size (15mmx15mm and 1mmx1mm) on the alumina substrate, and it calcinated after 10-minute desiccation at 120 degrees C, and calcinated with the continuous furnace for 10 minutes at the peak temperature of 850 degrees C.

[0020] When the size 15mmx15mm resistor was started with a diameter of 3mm in the shape of [thin] a disk using the ultrasonic cutter the whole substrate, Ar ion accelerated to 4kV with the ion grinder was irradiated from the alumina substrate side, the small hole was made and the thin field near the hole was observed with the acceleration voltage of 200kV with the JEM[by JEOL Co., Ltd.]-2000EX mold transmission electron microscope, the conductive particle distributed in the glass matrix was observed. Next, the electrical property of a size 1mmx1mm resistor was measured, and it became as it is shown in a table 2 about sheet resistivity, TCR, the noise, and ESD (electrostatic proof pressure). here -- TCR -- the rate of change by the room temperature and the difference with a resistance of 125 degrees C -- a table -- it is a thing the bottom and ESD shows the rate of change of the resistance after discharging 5 times at intervals of 1 second from a capacitor with a capacity of 200pF under the electrical potential difference of 1000V.

[0021] After putting in 15g of powder of an example diacid-ized rhenium (Re_2O_3), 5g of powder of a diacid-ized ruthenium (RuO_2), and 100 cc of water into the union process company MA-01 mold attritor mill with 0.1l. of steel balls with a diameter of 1/8 inch and mixing by agitator rotational frequency 100rpm for 5 hours, it filtered and dried and surface treatment rhenium oxide / diacid-ized ruthenium mixed powder was obtained. After this, the thick film resistor was produced like the example 1 by having been made from this mixed powder, and that electrical property was measured.

[0022] After putting in 15g of powder of example 3 rhenium oxide (Re_2O_3), 5g of powder of oxidization iridium (Ir_2O_3), and 100 cc of water into the union process company MA-01 mold attritor mill with 0.1l. of steel balls with a diameter of 1/8 inch and mixing by agitator rotational

frequency 100rpm for 5 hours, it filtered and dried and surface treatment rhenium oxide / oxidation iridium mixed powder was obtained. The organic vehicle which uses glass frit 16g, and the ethyl cellulose and the terpeneol of the presentation same to 4g of this mixed powder as an example 1 as a principal component was used as resistive paste so that it might become 30% of the weight of the whole. After this, the thick film resistor was produced like the example 1 by having been made from this resistive paste, and that electrical property was measured.

[0023] After putting in 15g of powder of example 4 rhenium oxide (Re 2O₃), 5g of powder of lead ruthenium pyrochlore (Pb₂Ru₂O₇-X), and 100 cc of water into the union process company MA-01 mold attritor mill with 0.1l. of steel balls with a diameter of 1/8 inch and mixing by agitator rotational frequency 100rpm for 5 hours, it filtered and dried and surface treatment rhenium oxide / lead ruthenium pyrochlore mixed powder was obtained. The organic vehicle which uses glass frit 16g, and the ethyl cellulose and the terpeneol of a presentation of 65.1%PbO-26.5%SiO₂-0.8%B-2O₃-7.6%aluminum 2O₃ to 4g of this mixed powder as a principal component was used as resistive paste so that it might become 30% of the weight of the whole. After this, the thick film resistor was produced like the example 1 by having been made from this resistive paste, and that electrical property was measured.

[0024] After putting in 15g of powder of example 5 rhenium oxide (Re 2O₃), 5g of powder of bismuth rhodium pyrochlore (Bi₂Rh₂O₇-X), and 100 cc of water into the union process company MA-01 mold attritor mill with 0.1l. of steel balls with a diameter of 1/8 inch and mixing by agitator engine-speed 100rpm for 5 hours, it filtered and dried and surface treatment rhenium oxide / bismuth rhodium pyrochlore mixed powder was obtained. In addition, the organic vehicle which uses glass frit 16g, and the ethyl cellulose and the terpeneol of the same presentation as an example 4 as a principal component was used as resistive paste at 4g of this mixed powder so that it might become 30% of the weight of the whole. After this, the thick film resistor was produced like the example 1 by having been made from this resistive paste, and that electrical property was measured.

[0025] The glass frit of the same presentation as an example 1 was mixed with the powder of an example of comparison 1 diacid-ized ruthenium (RuO₂) with V blender, 20g of powder with which a diacid-ized ruthenium is contained 10% was prepared, after this, the thick film resistor was produced like the example 1 by having been made from this mixed powder, and the electrical property was measured.

[0026] Mixing the glass frit of the same presentation as an example 4 with the powder of example of comparison 2 lead ruthenium pyrochlore (Pb₂Ru₂O₇-X) with V blender, 20g of powder with which lead ruthenium pyrochlore is contained 20% was prepared, and the rest produced the thick film resistor like the example 1, and measured the electrical property.

[0027] Mixing the glass frit of the same presentation as an example 4 with the powder of example of comparison 3 rhenium oxide (Re 2O₃) with V blender, 20g of powder with which rhenium oxide is contained 10% was prepared, and the rest produced the thick film resistor like the example 1, and measured the electrical property. The electrical property of the resistor obtained with each paste by the table 1 in the configuration of the paste of examples 1-5 and the examples 1-3 of a comparison is shown in a table 2.

[0028]

[A table 1]

The configuration of a paste Main electric conduction object Surface treatment component The surface treatment approach An electric conduction object and glass ratio of a frit -----
----- example 1 Re 2O₃ RuO₂ A ball mill 1:9 2 Re 2O₃ RuO₂ Attritor 1:9 3 Re 2O₃ 2OIr₃
attritor 2:8 4 Re 2O₃ Pb₂Ru₂O₇-X Attritor 2:8 5 Re 2O₃ Bi₂Rh₂O₇-X Attritor 2:8 Example 1 of a
comparison RuO₂ - - 1:9 2 Pb₂Ru₂O₇-X - - 2:8 3 Re₂O₃ - - 1:9 [0029]

[A table 2]

Electrical property of a resistor Sheet resistivity value TCR Noise ESD log (omega/**) (ppm/degree C) (dB) (%)

----- The example 1 4.22 - 248 2.5 -0.09 2 4.39 - 168 - 7.4 0.05 3 3.58 - 87 -
14.3 -0.64 4 4.26 - 159 - 4.0 -0.21 5 3.81 64 -11.6-0.10 Example 1 of a comparison 3.2862 -8.21.86
2 3.59- 48 -13.9 -1.55 3 10.26 Measurement improper off-limits - 10.93 [0030] If the electrical
property of the resistor produced in the above example and example of a comparison is seen, the

resistor by this invention It is the range correctable to a fitness value enough by addition of a little regulator although TCR is a little large to negative compared with the usual thick film resistor which used a diacid-ized ruthenium and ruthenium system pyrochlore. If ESD and the noise have the almost equivalent electrical property, what has a lower noise level is obtained depending on production conditions, therefore rhenium oxide passes through the surface treatment of the above-mentioned publication, it is clear that it can be used as an electric conduction object for resistive paste. However, if rhenium oxide is used as it is, without passing through surface treatment, as shown in the example 3 of a comparison for evaporation under baking, as for the electrical property, business as a resistor will not be accomplished.

[0031]

[Effect of the Invention] Since a rhenium can be substituted for most conductive powder raw materials according to this invention, without replacing the conventional ruthenium and lowering a property, a price can be reduced and the class and property of a product can be extended.

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(54)【発明の名称】 厚膜抵抗体形成用ペースト

(57)【要約】

【目的】 従来品と電気的特性がほぼ同じで、従来品に比べて安価な厚膜抵抗体形成用ペーストを提供する。

【構成】 導電性粒子とガラスフリット及び有機ビヒクルとで実質的に構成される厚膜抵抗体形成用ペーストにおいて、前記導電性粒子がルテニウム酸化物、イリジウム酸化物、ロジウム酸化物のうち一種又は二種からなる被覆層で粒子表面の一部又は全部が被覆されている酸化レニウム粒子であることを特徴とする厚膜抵抗体形成用ペースト。

【特許請求の範囲】

【請求項1】 導電性粒子とガラスフリット及び有機ビヒクルとで実質的に構成される厚膜抵抗体形成用ペーストにおいて、前記導電性粒子がルテニウム酸化物、イリジウム酸化物、ロジウム酸化物のうち一種又は二種からなる被覆層で粒子表面の一部又は全部が被覆されている酸化レニウム粒子であることを特徴とする厚膜抵抗体形成用ペースト。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、ハイブリッドICや厚膜チップ部品の抵抗体素子を形成するために使用されるペーストに関する。

【0002】

【従来の技術】 電子材料における厚膜抵抗体素子は、安価で手軽且つ高信頼性があることから広範に利用されているが、生産技術がほぼ確立している現在、益々高品質且つ廉価に供給出来るものが要求されるようになっている。この厚膜抵抗体は、厚膜抵抗体形成用ペーストを基板上に印刷して焼成するだけで、回路中の抵抗体素子を形成出来るものである。このペーストは、導電性粒子とガラスフリット及びそれらを印刷に適したペースト状にするために添加される有機ビヒクルから実質的に構成される。現状では殆どの場合、導電性粒子としては二酸化ルテニウム (RuO_2) かRu系パイロクロア ($\text{Bi}_2\text{Ru}_2\text{O}_7\text{-X}$ 、 $\text{Pb}_2\text{Ru}_2\text{O}_7\text{-X}$) が、ガラスフリットにはホウケイ酸鉛ガラス ($\text{PbO-SiO}_2\text{-B}_2\text{O}_3$) やアルミノホウケイ酸鉛ガラス ($\text{PbO-SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3$) 等のホウケイ酸鉛系ガラスが使われている。

【0003】 導電性粒子としてRu系酸化物が使われるのは、主として導電性粒子量に対する電気抵抗値の関係（ローディング曲線）がなだらかに変化するからである。ガラスフリットにホウケイ酸鉛系ガラスが用いられるのは、熱膨張係数がアルミナ基板のそれに近く、粘性や表面張力の温度依存性、 RuO_2 との濡れ性等がこのペースト系に適しているからである。この基本組成に加えて、抵抗値の温度係数（TCR）の調整、印刷性、レーザーによるトリミング性、焼成時の印刷ダレ性、基板との密着性、導体電極との反応性、コートガラスとの膨張係数の差、等を考慮して種々の添加物が加えられ、これまで非常に多種類のペーストが開発されてきた。

【0004】 電気特性とは別次元の問題として、Ru系抵抗ペーストの欠点として古くから認識されているのは、ルテニウム酸化物がガラスや通常の酸化物原料に比べて高価なことである。特性的にルテニウムに替わり得る元素としてイリジウムやロジウム等があるが、これらはルテニウムよりも更に高価である。ルテニウム酸化物の全体又は一部を電気的特性を低下させずに、これよりも安価な導電性粒子に代替できればコストの削減が出来

るが、これまでそのような有効な代替物は知られていなかった。

【0005】

【発明が解決しようとする課題】 本発明の課題は、従来品と電気的特性がほぼ同じで、従来品に比べて安価な厚膜抵抗体形成用ペーストを提供することにある。

【0006】

【課題を解決するための手段】 本発明は、導電性粒子とガラスフリット及び有機ビヒクルとで実質的に構成される厚膜抵抗体形成用ペーストにおいて、前記導電性粒子がルテニウム酸化物、イリジウム酸化物、ロジウム酸化物のうち一種又は二種からなる被覆層で粒子表面の一部又は全部が被覆されている酸化レニウム粒子であることを特徴とする厚膜抵抗体形成用ペーストにある。

【0007】 この厚膜抵抗体形成用ペーストの導電性粒子、ガラスフリット並びに印刷用有機ビヒクル及びこれら以外の添加物は、従来の厚膜抵抗体形成用ペーストと同様の配合割合で用いられる。

【0008】 本発明で使用する導電性粒子は、酸化レニウム (Re_2O_3 、 ReO_2 、 ReO_3 、 Re_2O_7 のいずれか) 粒子を主体とし、且つその粒子表面がルテニウム酸化物、イリジウム酸化物、ロジウム酸化物、のうち一種又は二種以上によりその全体又は一部分が被覆された構造であることを特徴とする。本発明でルテニウム酸化物とは酸化ルテニウム（即ち RuO_2 、 RuO_3 、又は RuO_4 ）やルテニウム系パイロクロア（即ち $\text{Pb}_2\text{Ru}_2\text{O}_7\text{-X}$ 、 $\text{Bi}_2\text{Ru}_2\text{O}_7\text{-X}$ 、 $\text{Ti}_2\text{Ru}_2\text{O}_7$ など）を含み、イリジウム酸化物とは酸化イリジウム（即ち Ir_2O_3 又は IrO_2 ）及びイリジウム系パイロクロア（即ち $\text{Pb}_2\text{Ir}_2\text{O}_7\text{-X}$ 、 $\text{Bi}_2\text{Ir}_2\text{O}_7\text{-X}$ 、 $\text{Lu}_2\text{Ir}_2\text{O}_7$ など）を含み、又ロジウム酸化物とは酸化ロジウム（即ち Rh_2O_3 、 RhO_2 、又は RhO_3 ）、及びロジウム系パイロクロア（ $\text{Pb}_2\text{Rh}_2\text{O}_7\text{-X}$ 、 $\text{Bi}_2\text{Rh}_2\text{O}_7\text{-X}$ 、 $\text{Ti}_2\text{Rh}_2\text{O}_7$ など）を含むものとする。

【0009】 ガラスフリットは通常の厚膜抵抗体形成用ペーストに用いられているホウケイ酸鉛ガラスを主体としたものであれば良く、通常はこの三元系にアルミナ、酸化亜鉛、カルシア、チタニア、酸化バリウム等を含む組成に修正されて使用される。

【0010】 本発明の導電性粒子は、蒸着、スパッタリング等で酸化レニウム粒子表面にRu又はIr又はRhの薄膜を形成し、これを加熱して酸化膜を形成する。更に乾式又は湿式のボールミル混合によっても得ることが出来る。例えば、ジルコニアボール等を攪拌媒体として使用し、分散溶媒の存在下若しくは存在なしに通常の水平型ボールミル混合を行っても良いし、又SPEX (Sytech Corporation) などの振動ミルや、アジテータ羽で強制的に電動攪拌するSzegvariのアトライターミル (Union Process Inc.) などの機械的圧力の高い混合ミルを用いても良い。

【0011】振動ミルやアトライターミルを用いる場合、酸化レニウム粉末に加えて、酸化ルテニウム、酸化イリジウム、酸化ロジウム、ルテニウム系パイロクロア、イリジウム系パイロクロア、及びロジウム系パイロクロアのうちの一種又は二種以上を混合し、セラミックやステンレス製の硬いボールを使用して、乾式又は水やアルコールを少量加えた湿式で強制攪拌混合を行う。

【0012】又乾式で行う場合や湿式でも加える溶媒量が少ない場合、導電性粒子が高価であることや、アジテータ羽による摩擦や攪拌性を考慮して、導電性粒子に加えるガラスフリットを予めこの工程で混合しても良い。

【0013】

【作用】酸化レニウムはそれ単独でガラスと混合して加熱すると途中で Re_2O_7 に酸化が進み、これが低温度（250℃）で昇華してレニウム成分が失われるため、高温で焼成した後は抵抗体としての導電性が殆どなくなってしまう。しかしルテニウム化合物、イリジウム化合物、又はロジウム化合物を蒸着或はスパッターで膜を付けてから、これらの膜を酸化させることにより、酸化レニウム粒子表面が大気やビヒクルと触れ合う部分が少なくなり、焼成中にレニウム成分の揮発が抑えられ、厚膜抵抗体形成用ペーストの導電性成分として使用することが可能となる。

【0014】又酸化レニウム粒子を酸化ルテニウム、酸化イリジウム、酸化ロジウム、ルテニウム系パイロクロア、イリジウム系パイロクロア、ロジウム系パイロクロア等の粒子と共にボールミル混合を行う場合は、酸化レニウム粒子の表面が細かい二酸化ルテニウムなどの粒子で覆われる。更に振動ミルやアトライターなど強力攪拌の伴ったボールミルで混合を施す場合には、一部のレニウム原子は酸素との結合を断ってメタルクラスタになったり、ルテニウム原子などと置換して酸化レニウム表面が $(\text{Re}, \text{Ru})\text{O}_2$ 等の構造へ変質することもある。

【0015】従って、焼成中にレニウム成分の揮発が抑えられると同時に、歪みを多く蓄えた酸化レニウム粒子表面層やクラスタ状態のメタルがガラス中への Re や Ru の拡散を促進し、導電性粒子の分散状態が良くなってノイズなどの電気特性にも好影響を及ぼす。

【0016】またガラス粒子を加えてこれと共にボールミル混合する場合には、導電性粒子に加わる機械的圧力により酸化レニウムや二酸化ルテニウムの凝集がとれてガラス粒子により分散性が良くなると同時に、高エネルギーミルを用いた場合には接触局所の温度が上昇し、この熱機械的効果によりレニウムやルテニウムの一部が極微細粒子又はクラスタとしてガラス粒子中に溶入する。このような特殊な微細構造をもつガラスフリットをペーストに用いると、抵抗体素子のノイズを低下させ耐電性を向上出来る。

【0017】以上のように、表面をルテニウム、イリジウム、ロジウムなどの酸化物で覆われた個々の酸化レニ

ウム粒子は電導度が下がることなく、又ペースト焼成時にはこれらの粒子からガラスマトリックスに向けてレニウムやルテニウムの拡散が通常ペーストと同等か又はそれ以上に行われるので、これを用いた抵抗体は酸化レニウムという安価な代替物質を用いながらも、分散性が上がってノイズが低減され良好な抵抗体特性を示す。

【0018】

【実施例】

実施例1

酸化レニウム（ Re_2O_3 ）の粉末15gと二酸化ルテニウム（ RuO_2 ）の粉末5g及びエチルアルコール8mlを、ジルコニアボール150gと共にプラスチック容器に入れ、水平ボールミル混合を7日間行った。これを濾過、乾燥して、表面改質酸化レニウム／二酸化ルテニウム混合粉を得た。この粉末をn-ブチルメタクリレート樹脂に包埋し、Reichert-Jung社製の超マイクローム（ULTRACUT-E）で粉末の断面スライスを含む樹脂片を作製し、これを日本電子（株）製JEM-2000EX型透過電子顕微鏡で加速電圧200kVで観察すると、酸化レニウム粒子の表面付近に二酸化ルテニウムと思われる別構造が観察された。

【0019】この粉末2gに重量%で（以下%は総て重量%を表す）55.4% PbO —24.7% SiO_2 —12.3% B_2O_3 —8.5% Al_2O_3 の組成のガラスフリット18g、及びエチルセルロースとテルピネオールを主成分とする有機ビヒクルを全体の30重量%となるように加えて、抵抗ペーストとした。これをアルミナ基板上に15mm×15mm及び1mm×1mmのサイズにスクリーン印刷し、120℃で10分乾燥後、ピーク温度850℃で10分の連続焼成炉で焼成した。

【0020】サイズ15mm×15mmの抵抗体は、基板ごと超音波カッターを用いて直径3mmの薄いディスク状に切り出し、イオン研磨機で4kVに加速した Ar イオンをアルミナ基板側から照射して小さな穴を開け、穴近くの薄い領域を日本電子（株）製JEM-2000EX型透過電子顕微鏡で加速電圧200kVで観察すると、ガラスマトリックス中に分散した導電性粒子が観察された。次にサイズ1mm×1mmの抵抗体の電気特性を測定し、面積抵抗、TCR、ノイズ、ESD（静電耐圧）については表2のようになった。ここで、TCRとは室温と125℃での抵抗値の差を変化の割合で表したものであり、ESDは1000Vの電圧下で200pFの容量のコンデンサから1秒間隔で5回放電した後の抵抗の変化率を示している。

【0021】実施例2

酸化レニウム（ Re_2O_3 ）の粉末15gと二酸化ルテニウム（ RuO_2 ）の粉末5g及び水100ccを、直径1/8インチのスチールボール0.1リットルと共にユニオンプロセス社MA-01型アトライターミル中に入れ、アジテータ回転数100rpmで5時間混合した後、濾

過、乾燥して、表面改質酸化レニウム／二酸化ルテニウム混合粉を得た。これ以降はこの混合粉を材料として実施例1と同様にして厚膜抵抗体を作製し、その電気特性を測定した。

【0022】実施例3

酸化レニウム (Re_2O_3) の粉末15gと酸化イリジウム (Ir_2O_3) の粉末5g及び水100ccを、直径1/8インチのスチールボール0.1リットルと共にユニオンプロセス社MA-01型アトライターミル中に入れ、アジテータ回転数100rpmで5時間混合した後、濾過、乾燥して、表面改質酸化レニウム／酸化イリジウム混合粉を得た。この混合粉末4gに実施例1と同じ組成のガラスフリット16g、及びエチルセルロースとテルピネオールを主成分とする有機ビヒクルを全体の30重量%となるように加えて、抵抗ペーストとした。これ以降はこの抵抗ペーストを材料として実施例1と同様にして厚膜抵抗体を作製し、その電気特性を測定した。

【0023】実施例4

酸化レニウム (Re_2O_3) の粉末15gと鉛ルテニウムパイロクロア ($\text{Pb}_2\text{Ru}_2\text{O}_7\text{-X}$) の粉末5g及び水100ccを、直径1/8インチのスチールボール0.1リットルと共にユニオンプロセス社MA-01型アトライターミル中に入れ、アジテータ回転数100rpmで5時間混合した後、濾過、乾燥して、表面改質酸化レニウム／鉛ルテニウムパイロクロア混合粉を得た。この混合粉末4gに65.1% PbO - 26.5% SiO_2 - 0.8% B_2O_3 - 7.6% Al_2O_3 の組成のガラスフリット16g、及びエチルセルロースとテルピネオールを主成分とする有機ビヒクルを全体の30重量%となるように加えて、抵抗ペーストとした。これ以降はこの抵抗ペーストを材料として実施例1と同様にして厚膜抵抗体を作製し、その電気特性を測定した。

【0024】実施例5

酸化レニウム (Re_2O_3) の粉末15gとビスマスロジ

ウムパイロクロア ($\text{Bi}_2\text{Rh}_2\text{O}_7\text{-X}$) の粉末5g及び水100ccを、直径1/8インチのスチールボール0.1リットルと共にユニオンプロセス社MA-01型アトライターミル中に入れ、アジテータ回転数100rpmで5時間混合した後、濾過、乾燥して、表面改質酸化レニウム／ビスマスロジウムパイロクロア混合粉を得た。この混合粉末4gに、実施例4と同じ組成のガラスフリット16g、及びエチルセルロースとテルピネオールを主成分とする有機ビヒクルを全体の30重量%となるように加えて抵抗ペーストとした。これ以降はこの抵抗ペーストを材料として実施例1と同様にして厚膜抵抗体を作製し、その電気特性を測定した。

【0025】比較例1

二酸化ルテニウム (RuO_2) の粉末と、実施例1と同じ組成のガラスフリットをVブレンダーで混合して、二酸化ルテニウムが10%含まれる粉末を20g用意し、これ以降はこの混合粉末を材料として実施例1と同様にして厚膜抵抗体を作製し、電気特性を測定した。

【0026】比較例2

鉛ルテニウムパイロクロア ($\text{Pb}_2\text{Ru}_2\text{O}_7\text{-X}$) の粉末と、実施例4と同じ組成のガラスフリットをVブレンダーで混合して、鉛ルテニウムパイロクロアが20%含まれる粉末を20g用意し、あとは実施例1と同様にして厚膜抵抗体を作製し、電気特性を測定した。

【0027】比較例3

酸化レニウム (Re_2O_3) の粉末と、実施例4と同じ組成のガラスフリットをVブレンダーで混合して、酸化レニウムが10%含まれる粉末を20g用意し、あとは実施例1と同様にして厚膜抵抗体を作製し、電気特性を測定した。実施例1～5及び比較例1～3のペーストの構成を表1に、各ペーストによって得られた抵抗体の電気特性を表2に示す。

【0028】

【表1】

ペーストの構成

主要導電物 表面改質成分 表面改質方法 導電物とガラスフリットの比

実施例1	Re_2O_3	RuO_2	ボールミル	1 : 9
2	Re_2O_3	RuO_2	アトライター	1 : 9
3	Re_2O_3	Ir_2O_3	アトライター	2 : 8
4	Re_2O_3	$\text{Pb}_2\text{Ru}_2\text{O}_7\text{-X}$	アトライター	2 : 8
5	Re_2O_3	$\text{Bi}_2\text{Rh}_2\text{O}_7\text{-X}$	アトライター	2 : 8
比較例1	RuO_2	—	—	1 : 9
2	$\text{Pb}_2\text{Ru}_2\text{O}_7\text{-X}$	—	—	2 : 8
3	Re_2O_3	—	—	1 : 9

【表2】

抵抗体の電気特性

面積抵抗値 TCR ノイズ ESD

【0029】

	$\log (\Omega / \square)$	(ppm/°C)	(dB)	(%)
実施例 1	4.22	-248	2.5	-0.09
2	4.39	-168	-7.4	0.05
3	3.58	-87	-14.3	-0.64
4	4.26	-159	-4.0	-0.21
5	3.81	64	-11.6	-0.10
比較例 1	3.28	62	-8.2	1.86
2	3.59	-48	-13.9	-1.55
3	10.26	測定不可	オフリミット	-10.93

【0030】以上の実施例と比較例で作製された抵抗体の電気特性を見ると、本発明による抵抗体は、二酸化ルテニウムやルテニウム系パイロクロアを使用した通常の厚膜抵抗体に比べるとTCRはやや負に大きいが少量の調整剤の添加で充分適性値に修正出来る範囲であり、ESDやノイズはほぼ同等の電気特性を有しており、又作製条件によってはノイズレベルはより低いものも得られ、従って酸化レニウムが上記記載の表面処理を経れば抵抗ペースト用の導電物として使用出来ることが明らか

である。しかしもし酸化レニウムが表面処理を経ずにそのまま使用されれば、焼成中の蒸発の為に比較例3に示されるようにその電気特性は抵抗体としての用を成さないものとなる。

【0031】

【発明の効果】本発明によれば、従来のルテニウムに替わって、特性を下げることなく導電性粉末原料の大部分をレニウムで代替出来るため、価格を低減でき製品の種類や特性を広げ得る。

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